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Occurrence and geochemistry of radium in water from principal drinking-water aquifer systems of the United States

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Abstract

A total of 1270 raw-water samples (before treatment) were collected from 15 principal and other major aquifer systems (PAs) used for drinking water in 45 states in all major physiographic provinces of the USA and analyzed for concentrations of the Ra isotopes 224Ra, 226Ra and 228Ra establishing the framework for evaluating Ra occurrence. The US Environmental Protection Agency Maximum Contaminant Level (MCL) of 0.185 Bq/L (5 pCi/L) for combined Ra (226Ra plus 228Ra) for drinking water was exceeded in 4.02% (39 of 971) of samples for which both 226Ra and 228Ra were determined, or in 3.15% (40 of 1266) of the samples in which at least one isotope concentration (226Ra or 228Ra) was determined. The maximum concentration of combined Ra was 0.755 Bq/L (20.4 pCi/L) in water from the North Atlantic Coastal Plain quartzose sand aquifer system. All the exceedences of the MCL for combined Ra occurred in water samples from the following 7 PAs (in order of decreasing relative frequency of occurrence): the Midcontinent and Ozark Plateau Cambro-Ordovician dolomites and sandstones, the North Atlantic Coastal Plain, the Floridan, the crystalline rocks (granitic, metamorphic) of New England, the Mesozoic basins of the Appalachian Piedmont, the Gulf Coastal Plain, and the glacial sands and gravels (highest concentrations in New England).

The concentration of Ra was consistently controlled by geochemical properties of the aquifer systems, with the highest concentrations most likely to be present where, as a consequence of the geochemical environment, adsorption of the Ra was slightly decreased. The result is a slight relative increase in Ra mobility, especially notable in aquifers with poor sorptive capacity (Fe-oxide-poor quartzose sands and carbonates), even if Ra is not abundant in the aquifer solids. The most common occurrence of elevated Ra throughout the USA occurred in anoxic water (low dissolved-O2) with high concentrations of Fe or Mn, and in places, high concentrations of the competing ions Ca, Mg, Ba and Sr, and occasionally of dissolved solids, K, SO4 and HCO3. The other water type to frequently contain elevated concentrations of the Ra radioisotopes was acidic (low pH), and had in places, high concentrations of NO3 and other acid anions, and on occasion, of the competing divalent cations, Mn and Al. One or the other of these broad water types was commonly present in each of the PAs in which elevated concentrations of combined Ra occurred. Concentrations of 226Ra or 228Ra or combined Ra correlated significantly with those of the above listed water-quality constituents (on the basis of the non-parametric Spearman correlation technique) and loaded on principal components describing the above water types from the entire data set and for samples from the PAs with the highest combined Ra concentrations.

Concentrations of 224Ra and 226Ra were significantly correlated to those of 228Ra (Spearman's rank correlation coefficient, +0.236 and +0.326, respectively). Activity ratios of 224Ra/228Ra in the water

samples were mostly near 1 when concentrations of both isotopes were greater than or equal to 0.037 Bq/L (1 pCi/L), the level above which analytical results were most reliable. Co-occurrence among these highest concentrations of the Ra radionuclides was most likely in those PAs where chemical conditions are most conducive to Ra mobility (e.g. acidic North Atlantic Coastal Plain). The concentrations of 224Ra were occasionally greater than 0.037 Bq/L and the ratios of 224Ra/228Ra were generally highest in the PAs composed of alluvial sands and Cretaceous/Tertiary sandstones from the western USA, likely because concentrations of 224Ra are enhanced in solution relative to those of 228Ra by alpha recoil from the aquifer matrix. Rapid adsorption of the two Ra isotopes (controlled by the alkaline and oxic aquifer geochemistry) combined with preferential faster recoil of 224Ra generates a 224Ra/228Ra ratio much greater than 1. The 228Ra/226Ra activity ratio was locally variable, and was generally lower than 1 (226Ra rich) in samples from PAs with carbonate bedrock, but was typically greater than 1 (228Ra rich) in PAs composed of unconsolidated sand.

The New York Times

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Drinking Water, And What Else?; From Wells In South Jersey Flow Radium, and Anxiety

By ANDREA KANNAPELL

LIKE most people in southern New Jersey, Catherine Rabbai learned about the water from news reports. The delicious drinking water from the well in the backyard of her two-story Pittsgrove home might have radium in it.

The first article on the subject was on the front page of The Philadelphia Inquirer on Aug. 9. Under the headline "Radium Tainting Water in N.J. Wells," it began: "Federal scientists have found widespread evidence of cancer-causing agents in the major source of drinking water for hundreds of thousands of people in South Jersey." The evidence, a report issued in June, was compelling: 33 percent of sampled wells showed levels of radium that exceeded Federal standards. In developed areas, the proportion went up to 65 percent.

As other newspapers around the country picked up the story, phone calls started flooding New Jersey's Bureau of Safe Drinking Water. "We couldn't keep up with the phone traffic," said Barker Hamill, the bureau chief.

Ms. Rabbai wasted no time: she found a lab certified to perform tests for radioactivity, Teledyne, in Westwood. She even got an extra testing kit for her neighbors.

"I am very concerned," Ms. Rabbai said, after the tests showed that her water registered as mildly radioactive. "We have the second-largest nuclear power company in the nation in New Jersey, and we have background radiation, radiation from the ground and from the sun. And this in addition makes me very concerned."

Over the last few weeks, more questions than answers about the radium seem to have emerged. And the answers themselves are not simple, involving hard sciences like physics, geology and hydrology, as well as the inner workings of scientific organizations and public bureaucracies. One thing that is clear: discoveries by New Jersey's scientists are changing the way the nation looks at -- and for -- radioactive contaminants in drinking water.

There is unquestionably radium floating around in South Jersey's most accessible aquifer, the Kirkwood-Cohansey, as indicated in the report that caused the recent furor, a June fact-sheet from the United States Geological Survey.

The radium is not industrial waste. It is what uranium and thorium in surface rocks turn into as they undergo the normal process of radioactive decay, losing protons and neutrons as they progress toward atomic stability, eventually becoming lead.

But the radium has been entering the aquifer in larger than normal quantities over the last 35 years. It is doing so, New Jersey's scientists have discovered, because of the overuse of agricultural and lawn fertilizers, lime, road salt and other materials that either loosen the radium's grip on the rocks in which it occurs, or further acidify the already acidic aquifer, which keeps the radium from resolidifying and attaching itself to other rocks.

Fearsome Carcinogen Or Trivial Trace?

Not everyone is afraid. Mark Malench, a 38-year-old Vineland farmer, hasn't tested his well in 15 years.

"I don't think it's anything to worry about," he said of the radium. "It's like getting stressed out about being 100 feet away from someone smoking a cigarette. When the person is smoking a cigarette and the people 100 feet away start dropping dead, then I'll worry."

But for many people, the mere mention of the word radium draws space-age shivers of terror -- especially in a state with relatively high overall cancer rates (183 deaths per 100,000 people annually), at least one suspected cancer cluster, and an acknowledged problem with radon, the radioactive gas that seeps into basements. Scientists, fascinated by radioactivity in general, can offer detailed accounts of radium's behaviors and effects. But how dangerous is it?

Chemically, the problem is simple. Radium is structurally similar to calcium, so the body absorbs it into bones. There, its radioactive characteristics determine its threat.

Radium, like many of the 92 natural elements in the periodic table, comes in varieties -- isotopes -- that have slightly different radioactive properties depending on the mass in each atom's nucleus. Those properties determine the danger.

An isotope is called radioactive if it ejects particles in its progression toward a stable inner structure. When the ejected particles are a combination of protons and neutrons from the atom's nucleus, the emission is called alpha radiation. Alpha emitters are dangerous only if they are ingested or inhaled, because the particles do not have enough energy to penetrate skin. Once inside the body, the particles damage tissues.

There are two radium isotopes that have been of concern in drinking water. Radium-226, derived from uranium, is an alpha emitter associated with cancers of the nasal sinuses. Some of the dangers of radium-226 were established by women who painted the illuminated dials on wristwatches during World War I, in New Jersey and other states. Many "lip-pointed" their brushes, ingesting some of the radium-226 in the paint. And many died of cancer as a result.

The other isotope is radium-228. It emits beta radiation -- electrons -- but its particles are so small they do less tissue damage. The problem is that, as radium-228 builds up in the body, it decays into alpha emitters.

Someone who drinks, every day for 70 years, two liters of water that registers 5 picocuries (11 radioactive decays per minute) per liter has about a 1 in 10,000 chance of getting bone or sinus cancer. At that level or above, the Federal Environmental Protection Agency says, the water should be considered dangerous.

This all sounds frightening. But that danger is far less than that of getting cancer from more mundane factors, according to the American Cancer Society.

"Tobacco represents the most dominant risk for cancer that this country is threatened by," said Joann Schellenback, a spokeswoman. "Other than that, our diets, which are high fat, low fiber, with not enough fruits and vegetables."

The society estimates that 4,300 Americans in 10,000 will develop cancer at some point in their lives, and that about half will die of the cancer. Those figures are slightly misleading because they incorporate today's extended life spans of 85 years, and therefore include the deaths of many elderly people. They still make a powerful contrast to dangers of radium.

The radium is also easily removed, with a simple water-softening unit. "The fact that radium acts like calcium is, from the treatment perspective, good," said Mr. Hamill, the chief of the drinking water bureau.

And many wells may already have the units. Norman Primost, the president of the New Jersey Ground Water Association, a professional organization for drillers, geologists and other water-supply workers, believes that at least 50 percent and as many as 90 percent of the wells in southern New Jersey use water softeners to remove iron.

If a well shows significant alpha radioactivity, the Bureau of Safe Drinking Water suggests that homeowners consider installing a water softening unit ($600 to $800); an ion-exchange water treatment system (also $600 to $800) or a reverse osmosis system at, say, the kitchen sink ($100); hooking up to a municipal water supply, where the wells are usually deeper, or drilling a deeper well.

New Jersey water experts say they don't mean to play down the radium issue, but they believe that mercury contamination from pesticides and other manmade sources might be more significant.

Until 1988, no one suspected that southern New Jersey had a radium problem of any size at all. The focus was on northern New Jersey, where large quantities of uranium and thorium are tied up in 200-million-year-old granite and metamorphic rocks.

Southern New Jersey has relatively little of radium's parent elements, geologists say. It is mostly a plain composed of ancient layers of coastlines. Those layers are now aquifers, strata of water-soaked sand and gravel that feed wells and streams, and that, deep underground, press the ocean back, keeping ruinous saltwater out.

Water flows slowly -- perhaps a few dozen feet a year -- through the aquifers toward wells and streams. In Atlantic City, the water comes from wells drilled hundreds of feet deep; what wets gamblers' whistles fell as rain some 25,000 years ago.

The Bridgeton Formation, a thin, broken layer of sediments from the ancestral Hudson River, contains a good deal of uraniam and thorium.

But the thinking was, explained Zoltan Szabo, a research hydrologist with the U.S.G.S, that "only places with a lot of uranium or thorium in the rock would have a problem. But that didn't take into account the water chemistry. It turns out that it's not just how much is in the rock, but also on if the conditions are right for it to dissolve."

And in the south, the chemical environment -- the water loaded with fertilizers and other materials that was percolating through the rock and sinking through the aquifer -- was just right, Mr. Szabo realized. In one paper in 1995 and two in 1997, he explored the possibility that radium was leaching rapidly out of the coastal plain, finding ever more evidence of a problem.

The radium is not everywhere. The water moves through the aquifers in a network of pathways the experts describe as a twisted bundle of straws. Radium might wash out of a bit of Bridgeton rock and taint a well hundreds of feet away, while a closer well shows no sign of trouble.

Locally, Mr. Szabo's work prompted the New Jersey Department of Environmental Protection, which has financed much of the U.S.G.S.'s radium research, to issue repeated recommendations that private well owners have their water tested. The department published a booklet last year, baldly titled, "A Homeowner's Guide to Radioactivity in Drinking Water," which listed laboratories certified to gauge radioactivity. It is available from the department's Bureau of Safe Drinking Water, CN-426, Trenton, N.J., 08625; (609) 292-5550.

Nationally, the work has persuaded the Environmental Protection Agency and the Geological Survey to revisit their research. The results will be incorporated into new standards the E.P.A. plans to release in November 2000.

The new testing includes another New Jersey discovery, for which data is still being analyzed: there is a third radium isotope in the water, radium-224.

Atomic longevity is measured in half-lives, the time it takes for half of some quantity of an element to decay. Radium-226 has a half-life of 1,600 years. Radium-228's half-life is nearly six years. Radium-224 has a half-life of less than four days. No one looked for it because the assumption was that it would decay before it could dissolve into water. The assumption was wrong.

That came to light last spring, when scientists from several state agencies were trying to understand why the Toms River area has registered about 100 cases of childhood cancer in recent years, many more than, statistically, it should have.

During testing for all kinds of potential causes, water samples from Toms River were rushed through labs. Alpha radiation levels were so high, the scientists at first thought the tests must have been botched. (Radiation is not known to be associated with the kinds of cancers in Toms River.)

When repeated readings were high, Mr. Szabo and Dr. Bahman Parsa, who is the head of the state Department of Environmental Protection's radiation lab, came up with a suspect: a short-lived isotope.

Dr. Parsa retired to his lab, and began testing and retesting the same sample of water, getting a continuous picture of the drop-off of alpha radiation that exactly matched the half-life of radium-224.

Little Attention To Previous Reports

The simple fact of carcinogenic radiation in an aquifer that may be tapped by as many as 200,000 private wells seems shocking. How was it that the information leaped out of headlines more than a month after the June U.S.G.S. report was released?

Frederick Cusick, one of two Philadelphia Inquirer reporters who wrote the original article, said that the Geological Survey's report had not been publicized. He said that his co-writer, Maureen Graham, only heard about the findings in a telephone conversation with someone at the Geological Survey.

"We looked at the report," Mr. Cusick said, "and saw that it had more than twice the sampling of any previous report, and that it showed greater contamination than had been shown before."

And indeed it did.

Mr. Hamill, the chief of the drinking water bureau, admitted that he did not send the U.S.G.S. report any alerts to county health officials.

But the sampling had been undertaken in part because of Mr. Szabo's work, and at the Geological Survey and the Department of Environmental Protection, the findings were merely a stronger version of what they already knew. Prior reports had received little attention, not since the radium issue was first broached around 1990.

That's when Jane Nogaki, a Pinelands resident, had her well tested. A spokeswoman for the New Jersey Environmental Federation, an advocacy and watchdog group, she found radioactive levels near, but not exceeding, Federal standards.

"But I didn't feel comfortable, with two small children," she said. Radium is a bigger threat to the young, whose bones are still forming. To tap safer water, she dug 350 feet down into the Wenonah-Mount Laurel aquifer, at a cost of $5,000.

The recent report, she said, wasn't news to her.

Between the lack of urgency at the U.S.G.S. and the drinking water bureau -- and summer vacations of distribution staff -- the report was limping slowly out to state officials and to other U.S.G.S. offices.

Now they all realize that the prior D.E.P. alerts were easy to dismiss, and the prior Federal reports were long, jargon-filled streams of -ides and -opes and -ivities, barely accessible even to other hydrologists and geologists.

The June report, thanks to a new focus at the Geological Survey on frequent, reader-friendly updates, is a glossy, six-page fact sheet with clear maps and charts, written to be read by general readers.

"This was put together as a more useful document to communicate with elected officials and the concerned public," said Eric J. Evenson, the New Jersey district chief for the U.S.G.S. "And of course the concerned public has grown quite a bit lately."

Photos: (Laura Pedrick for The New York Times)(pg. 1); Testing drinking water at Teledyne Environmental Services in Westood, above. If significant levels of radium are found, there are several remedies like water softening units in wells or filters at home or using water from a deeper well. (Frank C. Dougherty for The New York Times)(Norman J. Lono for The New York Times) Map/Chart: "Breaking Down Ancient Elements" Atop the sandy layer that covers most of southern New Jersey lie packets of million-year-old river sedements called the Bridgeton formation, which is relatively rich in uranium and thorium, elements that naturally decay into radium. Acid rain, fertilizers, lime and road salt encourage the radium to dissolve out of the Bridgeton formation and to enter the water in the area's topmost acquifier, the Korkwood-Cohansey. Water from some wells that tap into this aquifer show radium levels that exceed Federal maximums. (Source: U.S. Geological Survey)(pg. 1) Diagram: "To Fetch a Pail of Water" There are multiple aquifers -- layers of water-soaked sand and gravel -- in southern New Jersey. They are tilted down to the east and separated by layers of clay, the remains of beaches from the last 100 million years. Naturally occurring radium has been leaching into the uppermost aquifer, the Kirkwood-Cohansey. Around Camden, shallow wells (60 to 100 feet deep) reach into the Potomac-Raritan-Magothy aquifer, but from Pittman eastward, they tap the Kirkwood-Cohansey, where radium has been found in comparison, in Berlin, it would take a 310-foot well to reach into the next deeper aquifer, the Wenonah-Mount Laurel aquifer. (Municipal and private wells)(pg. 7) "How a Problem Grows" Some radium dissolve into the Kirkwood-Cohansey aquifer even without the encouragement of uranium-rich rocks or agricultural activities. But, according to data collected from 1988 to 1986, those factors, especially when they occur together, increase the problem. (Source: United States Geological Survey)(pg. 7)
